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OPERATION OF A CASCADE AUTOCLAVE TO STUDY THE LIQUEFACTION OF WOOD CHIPS

RENEWABLE ENERGY BRANCH

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1.2 PREFACE

The results of several experimental runs using a cascade autoclave unit for the liquefaction of poplar wood chips are presented. Necessary modifications to the original unit are also outlined. The design basis of the system, procurement of component parts, construction and trial operation of the unit were described in the final report for 1985 (ref.1).

The objective of this study is to develop a continuous process for the production of an organic liquid which can then be processed using traditional chemical engineering operations. The identification and optimization of process variables and product analysis are steps towards this goal.

This system is, we believe, the first designed specifically to liquefy chips using steam alone at such temperatures. It is significant since cost considerations preclude the use of dry and powdered woods. In addition no catalyst or reducing gas is involved in the liquefaction.

The report will be of interest to those working in the field of thermal biomass liquefaction, since it illustrates that commercial-sized wood can be liquefied using steam at sufficiently high temperatures. Because of the high pressure and temperature involved, precautions must be taken to avoid injury due to unexpected leaks of steam from fittings and valves.

1.3 ABSTRACT

The Cascade Autoclave System for the liquefaction of poplar wood chips designed and constructed in the first phase has been successfully operated after further modifications. Some parameters involved in operating the system were studied, and data was collected and analysed. IEA poplar wood chips were liquefied using high temperature (330-355 C)/high pressure steam. This is significant, since feed stocks for such processes will invariably contain some water, in addition to being in chip form.

The system consists of a 1.5 inch (3.81 cm) I.D., 600 mL cylindrical reactor vessel supported vertically. In operation, a mesh basket containing up to 100 g of poplar wood chips (dry basis) is introduced through the upper ball-valve to the nitrogen purged, preheated reactor. After valve closure, steam is immediately injected. The steam valve is closed and after two minutes, the contents are discharged through a cooling lock. The product is collected in the form of acetone-free oil, acetone wash oil, aqueous products (solids and liquids), and gas. The 'oil' is almost all acetone soluble, and softens at just over 50 C. As the reaction temperature is increased, the amount of aqueous phase solids and acetone-insolubles decrease.

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1.5 EXECUTIVE SUMMARY

A cascade autoclave reactor was modified and operated successfully to produce acetone-soluble oil from wood chips. The main objectives of these runs were to get acquainted with the sequential and safe steps of operation, identify process variables and their importance in the liquefaction, and generate data for analysis.

For a particular run, a mesh basket containing 100 g of IEA poplar wood chips was inserted into the nitrogen-purged reactor (preheated to 390°C- 400°C). The reactor's inlet, outlet and vent valves were sealed, and steam was injected for a desired span of time (usually 7 seconds). After 2 minutes of reaction time, the contents of the reactor were cooled in the product letdown lock for 30 seconds and then discharged into the product receiver. The product oil solidified on cooling and could be readily separated from the aqueous products. The volume of gas produced was determined using a water displacement system.

The temperatures of the reactor top, middle, and bottom were recorded for each run. The products received as acetone free oil, wash oil (recovered from acetone used to clean the unit), aqueous phase liquid and solids, and acetone insolubles were

separated and analysed. Elemental composition of oil products, total carbon of the aqueous phase, and gas composition of a single run were determined in order to make a carbon balance. The oil consisted of approximately 69 % carbon, 6 % hydrogen, and 25% oxygen (by difference). The oil softened over 50°C and was acetone soluble.

When the reactor is heated up, successive runs can be made depending on the availability of steam in the steam generator, thus making the system semi-continuous. A high pressure pump available at our disposal can be used to make up the lost water in the steam generator. Besides wood chips, the reactor can also be used to study liquefaction of larger chips (up to 3.5 cm diameter and 64 cm long).

The conclusions derived from the present study are as follows: (a) the product distribution was a function of steam and reactor temperatures, steam injection and reaction times, and water level in the steam generator, (b) reducing the steam temperature below 335°C resulted in incomplete conversion of the wood, (c) increasing the steam temperature from 335°C to 355°C decreased yield of acetone insolubles and aqueous phase solids, (d) analysis of a single run showed 46 % oil yield (acetone soluble), on a dry mass basis, containing 64.3 % of

the total carbon output, the boiling range of the oil was 75°C and 575°C with 60 % distilling below 405°C (which is the upper boiling temperature for heavy gas oil, (e) reducing the steam injection time from 15 to 7 s did not change the oils produced as shown by comparing elemental analysis and boiling point distributions. Further reduction to 2-3 s of steam injection resulted in incomplete conversion of the wood. and (f) it was not necessary to wet the wood chips prior to a run.

The system should be upgraded to allow continuous recording and storing of thermocouple temperatures and desired pressure. Runs should be made with green or dry wood in the form of chips or stick. We are in the process of replacing the present low volume (122 mL) product receiver with a higher volume one (300 mL). The reactor outlet valve also needs to be replaced with a ball valve to allow complete discharge of the products. A level controller is required to keep a constant water level in the steam generator if sequential runs are to be made.

Considering the overall objectives and present achievements, the work so far has been very successful. The concept of liquefying wood chips in a cascade autoclave by injecting steam has been verified. Some of the major variables involved have been identified and studied. The importance of adding a data

acquisition system, a new product cooler, and a reactor outlet valve are also recognized.

The system is still in the preliminary stage of optimization and thus requires further studies to develop a continuous process for liquefaction.

1.6 RÉSUMÉ

On a modifié et exploité avec succès un réacteur autoclave en cascade pour produire de l'huile soluble dans l'acétone, à partir de copeaux de bois. Les divers essais visaient surtout à établir l'ordre et le niveau de sécurité des étapes d'exploitation, à déterminer les variables du procédé et leur importance dans le processus de liquéfaction ainsi qu'à produire des données en vue d'effectuer des analyses.

Pour un essai particulier, un panier à mailles contenant 100 g de copeaux de bois de peuplier normalisés par l'Agence internationale de l'énergie (AIE) est introduit dans le réacteur purgé à l'azote (préchauffé à une température de 390° C à 400° C) les valves d'admission, d'échappement et de ventilation du réacteur sont obturées et de la vapeur est injectée pendant une durée préétablie (habituellement 7 secondes) après une réaction de 2 minutes, on laisse refroidir le contenu du réacteur pendant 30 secondes dans le compartiment de détente du produit, puis on le déverse dans le récipient prévu à cet effet l'huile produite se solidifie en refroidissant et peut facilement être séparée des produits aqueux; on détermine le volume de gaz produit à l'aide d'un compteur volumétrique à déplacement d'eau.

À chaque essai, on enregistre les températures des parties supérieure, centrale et inférieure du réacteur. Les produits obtenus sous forme d'huile sans acétone, d'huile de rinçage (provenant de l'acétone utilisée pour nettoyer le réacteur), de liquides et de solides de la phase aqueuse, et de produits insolubles dans l'acétone, sont séparés et analysés. Afin d'obtenir un bilan du carbone, on a déterminé, pour un essai donné, la composition élémentaire de l'huile, la quantité totale de carbone produit dans la phase aqueuse et la composition des gaz. L'huile produite se compose d'environ 69 % de carbone, de 6 % d'hydrogène et de 25 % d'oxygène (par soustraction). L'huile devient plus liquide à une température supérieure à 50° C et est soluble dans l'acétone.

Le réacteur une fois réchauffé, il est possible d'effectuer des essais successifs à condition d'obtenir suffisamment de vapeur à partir du générateur; le système peut alors être mis en opération en mode semi-continu. On peut utiliser une pompe à haute pression pour remplacer l'eau perdue dans le générateur de vapeur. On peut également se servir du réacteur pour étudier la liquéfaction de plus gros copeaux de bois (jusqu'à 3,5 cm de diamètre et 64 cm de longueur).

Voici les conclusions découlant de la présente étude: a) la distribution des produits est fonction des températures de la vapeur et du réacteur, de la durée de l'injection de vapeur, du temps de réaction et du niveau d'eau dans le générateur de vapeur; b) la réduction de la température de la vapeur au-dessous de 335° C donne lieu à une conversion incomplète du bois; c) l'augmentation de la température de la vapeur de 335° C à 355° C entraîne une réduction du volume des produits insolubles dans l'acétone et des solides de la phase aqueuse; d) pour un essai donné, la production d'huile a été de 46 % (soluble dans l'acétone), par rapport à la matière sèche, correspondant à 64,3 % de la production totale de carbone; le point d'ébullition de l'huile a varié entre 75° C et 575° C, et 60 % de la distillation a eu lieu au dessous de 405° C (ce qui correspond à la température maximale d'ébullition du gasoil lourd); e) la réduction de la durée d'injection de vapeur de 15 secondes à 7 secondes n'entraîne aucun changement dans les huiles produites comme on le constate en comparant l'analyse élémentaire et les distributions du point d'ébullition. Si l'on réduit encore la durée d'injection de vapeur à 2 ou 3 secondes, la conversion du bois est alors incomplète; f) il n'est pas nécessaire de mouiller les copeaux de bois avant les essais.

Il convient d'améliorer le procédé pour permettre la lecture continue et la mise en mémoire des températures du thermocouple et de la pression. Pour les essais, on devrait utiliser du bois vert ou du bois sec sous la forme de copeaux ou de bâtonnets. Nous remplaçons actuellement le petit récipient (122 mL) par un plus gros (300 mL). Nous comptons aussi remplacer la valve d'échappement par une valve sphérique qui permettra le

déversement complet des produits. Si l'on compte effectuer des essais séquentiels, il faudra installer un régulateur pour maintenir le niveau d'eau constant dans le générateur de vapeur.

Compte tenu des objectifs globaux et des réalisations, les essais ont remporté un franc succès jusqu'à présent. Le concept de la liquéfaction de copeaux de bois dans un autoclave en cascade, par injection de vapeur, a été vérifié. On a établi certaines des variables les plus importantes mises en jeu et on les a étudiées. On reconnaît également qu'il est important d'ajouter un système d'acquisition de données, un nouveau réfrigérant du produit et une soupape d'échappement.

On en est encore au stade préliminaire de l'optimisation du procédé; pour mettre au point un processus continu de liquéfaction, il faudra poursuivre les études.

2.1 INTRODUCTION

This study is an expansion of our previous work on the liquefaction of single wood chip using steam at high temperature and pressure (ref..2). In the previous study, a single-wood chip (approx. 1 g) with water was subjected to rapid aqueous pyrolysis (330-350°C) inside a small tube type reactor (10 mL) resulting in complete conversion to acetone-soluble oil, aqueous-soluble organics and gases. Steam entered the chip causing it to swell and physically disintegrate. In these experiments, the amount of water was limited to that added at the beginning of the run, and when water/wood ratios were low (Approx. 1) the liquid phase disappeared from the reactor as the wood swelled. As the wood broke down the liquid water phase reappeared. The product oil was reasonably stable except at low water/wood ratios when char was formed from the oil. The conclusion was drawn that steam was primarily responsible for liquefaction, but liquid water was required for stabilization of the product.

The results of the above findings prompted studies into the feasibility of converting commercial sized poplar chips into usable fuels and chemicals. A cascade reactor unit (600 mL) capable of holding 100 grams wood chips (dry basis) was developed. The design of the system, procurement of the component

parts, construction and trial operation of the unit were presented and described in the final report for 1985 (ref. 1).

The following modifications were made after the initial trial operation of the unit:

(1) The reactor outlet ball-valve leaked and was replaced by a port valve having higher temperature/pressure rating.
(2) Because of a large temperature gradient within the reactor, much condensate was produced. To prevent this, a brass heating block was added to heat the bottom exit line connecting the reactor and the reactor outlet valve.
(3) The cold water cooling line on the product cooler was replaced with a hot water line to avoid solidification of the oil prior to discharge . Low pressure steam is also available.
(4) The manually operated nitrogen inlet valve was converted to air operation to further improve operation safety.

2.2 OBJECTIVES

The major objective of this work was to identify and optimise the process variables involved in the successful operation of the cascade autoclave liquefaction unit. This required the

generation of engineering and chemical data for analysis (temperature and pressure profiles, material balances, and product yields).

2.3 METHOD

2.3.1 EQUIPMENTS

The following integral component parts of the system are in use:

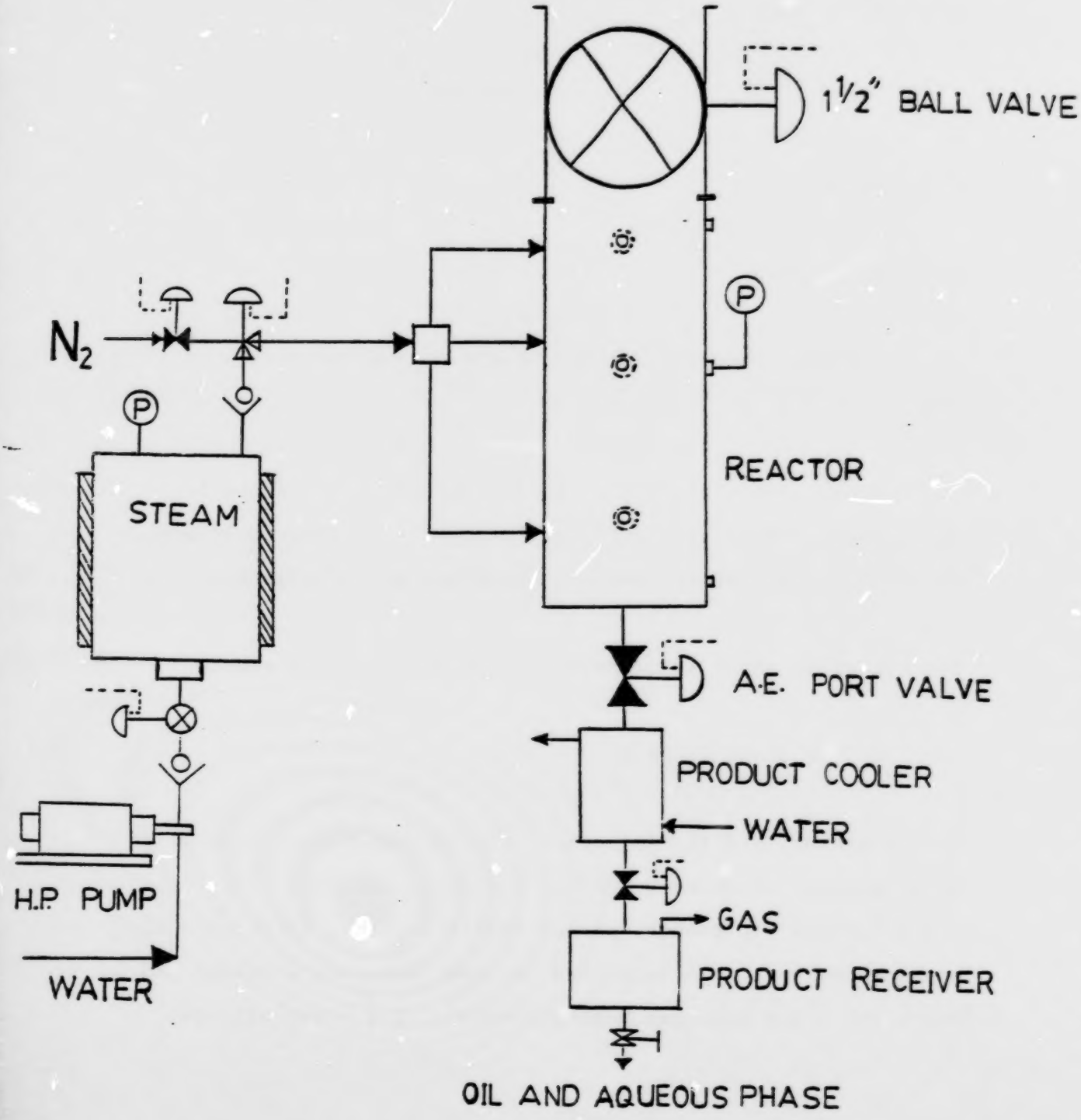
(a) a steam generator; (b) a reactor(cascade); (c) a reactor inlet valve; (d) a reactor outlet valve; (e) a product letdown lock and collector; (f) control panel and safety systems;

The system is shown schematically (not to scale) in Figure 1.

(a) The Steam Generator

The generator is a 2L (Autoclave Engineering) vessel capable of holding steam at or over 350°C. The steam transfer line, from the autoclave top flange, passes vertically to a three way air operated valve. This valve has two open ends and a closed end where the steam line has been connected. The steam/nitrogen

FIGURE- 1 CASCADE UNIT FOR WOOD CHIPS LIQUEFACTION



distribution line separates into three injection lines. The nitrogen purge line having an air operated valve is connected at the one open end of the 3-way valve. Presently, the steam generator is being filled manually with water. We have a Milton Royal high pressure water pump at our disposal which is capable of charging water against pressures in excess of 5000 psi. This pump, with appropriate level controller in use, could be very advantageous when making several sequential runs. The latter are possible since the steam remaining after the discharge of the products, can be removed through the vent line. It would thus be possible to make successive runs without cooling the system.

(b) Reactor

The reactor is a ss-316 vessel 1.5 inches (3.81 cm) I.D., 3 inches (7.62 cm) O.D., and 21 inches (53.34 cm) long, capable of holding in it a mesh basket containing 100 grams of wood chips. The reactor rating has been set at 3500 psi (24.1 MPa) at 350°C. THP Inc. of Montreal verified our design specifications, then constructed and hydrostatically tested the reactor as required by the appropriate ASME code.

The top section of the reactor is welded to an Oteco hub which facilitates attachment of a 3.81 cm inlet ball-valve with the help of a matching hub, a seal ring and clamps. The bottom

exit line of the reactor has been coned and threaded to fit a 2.54 cm stainless steel nipple which connects to the product discharge valve.

The reactor is provided with 8 holes to take 1/4 inch AE slim line connectors and one hole for 1/4 inch NPT connector. In use, the three holes on the left hand side (facing the reactor) are used for steam/nitrogen lines. The middle hole (1/4 inch NPT) on the front face and the bottom and top holes on the right side are used for thermocouples (1/8 inch). The upper hole on the front face is used for a rupture disc (3000 psi, 20.67 MPa), and the middle hole on the right hand side is used for a pressure gauge. The remaining hole is being used for venting the reactor. This hole could also be used for a pressure transducer to monitor the reactor pressure during the run.

The reactor is supported near its base by a split ring spot welded to a support plate. This ring also supports a metal plate on which the reactor insulation, in the form of ceramic brick, is stacked up to the neck of the reactor. The brick is cut and fitted to the external contours of the reactor.

The reactor is heated by two 6 feet long (1/8 inch O.D.) heaters joined in parallel. These are coiled around the reactor, and held close to the reactor by four steel strips and

eight circlips. The maximum power drawn by the heater is 4 KW. The coils are operated through a temperature controller. With all lagging in place, the reactor can be brought to a temperature of 365 C in 70 minutes.

(c) The Inlet Valve

The inlet valve is a 1.5 inches (3.8cm) I.D. Mogas ball valve type (ANSI # 2500 Series) and is rated at 3600 psi (24.8 MPa) at 370°C. The valve is joined to the reactor by a matching "Oteco" hub and is supported on the frame by two brackets. The controller is air operated via a solenoid valve. The valve and the controller weigh 68 kg and are attached to a pulley system to facilitate removal from the reactor when necessary.

The valve is insulated from excessive heat loss by three layers of 1.5 inches (3.8 cm) thick glass wool. Thus heat losses are limited primarily to conduction through the inlet and controller.

(d) Reactor Outlet Valve and Block Heater

The outlet from the reactor and inlet to the product cooler is connected by an Autoclave Engineering medium pressure port valve (.562 inch orifice size), Series 20 SV, and rated at 17000 psi (117.2 MPa) at 350°C. This valve, air operated

through a solenoid valve is a replacement of the previously used Crosby 0.5 inch I.D. ball valve which leaked at high temperature and pressure.

A brass block heater consisting of two equal sections to hold the one inch O.D. product exit line (nipple) has been made. Four 600 watt cartridge heaters were placed in the heater body. The rate of heating was controlled using a variac. A thermocouple placed in the middle of the heated block monitored temperature of the nipple's outside body.

(e) Product Let-Down Lock

The present cooling lock is 20 inches (50.8 cm) long and has an internal volume of 122 mL. Hot water is circulated through an external jacket to keep the oil in liquid form. A low pressure steam line is also available to cool down the product if required. The cooled product can be discharged through a horizontal and then vertical line into a glass product collector. The collector has a liquid discharge line at the bottom and a vent at the top for gas discharge or collection.

(g) Control Panel and Safety System

The control panel is located in an adjacent room to the system.

The panel contains main switches as well as switches to open and close various valves. A single digital readout only allows the readout of one thermocouple at a time - as determined by the multiposition switch mounted on top of the control panel. There are three temperature controllers connected to the control panel; one each for the steam generator and reactor heaters, and one for the solenoid valve which control the cold water flow to the cooling coil of the steam generator (upper temperature control).

The unit is located inside an explosion proof room. To avoid any accident due to sudden release of steam, the equipment has been provided with an electrical override workable with the help of an electromechanical device. The shaft of the inlet valve actuator has been provided with an extension arm. When the valve is fully closed, the arm activates a microswitch. If this switch is not activated, then the steam inlet will not open. The equipment is also designed such that, (a) the main inlet valve can not be opened if the steam inlet is open, and (b) the bottom product discharge valve can not be opened when reactor outlet valve is open (and vice versa). The override does not, however, prevent the accidental discharge of the reactor contents to the atmosphere. To avoid this possibility, the main inlet valve is a keyed switch and can only be operated if the key is inserted.

Finally `plexiglas' sheeting is installed in locations where sudden leaks could expose operators to high tempemperature and pressure steam.

2.3.2 MATERIALS

The system has been designed to study liquefaction using steam and wood chips/sticks with various dimensions. The wood could be dry, wetted or even green. Green logs are being supplied by the Ministry of Natural Resources of the Ontario Government. So far, IEA poplar wood chips, both dry and wetted have been used.

2.3.3 OPERATION

A mesh basket was filled with 100 grams of IEA poplar wood chips (approx. 8 % moisture). For runs with wetted wood chips, the loaded basket was inserted in water for 15 - 20 minutes. The initial and final weight of the basket was recorded. THe steam generator was filled with the desired amount of deionised water (reverse osmosis).. With the steam generator temperature raised to the desired point (330-355°C) and the reactor temperature at 390°C - 400°C, the basket was inserted through the reactor inlet valve to the nitrogen purged reactor. Care was taken to ensure that the basket cleared the

rotating ball of the valve. The nitrogen flow was stopped. The inlet valve was closed and steam immediately was injected (usually for 7 seconds). After 2 minutes of residence time, the products were discharged through the outlet valve to the product letdown lock where hot water was circulating through the cooling jacket. After approximately 30 seconds the lock outlet valve was opened and the products flowed into the product receiver. The product collection cycle was repeated as many times as necessary and the system cooled. A water displacement system connected to the product receiver was used to determine the volume of gas produced.

The reactor was opened and the basket, which has a loop handle on the top, was removed using a hook. The basket was empty and had only small amount of residue attached to it. The interior surface of the reactor was found to be clean initially, but began to foul after subsequent runs.

The reactor,lock system, and basket were washed with acetone to recover any remaining products and then weighed to quantify adhering residue. The reactor was cleaned further with water and steam befor the next run.

2.3.4 Product Separation and Analysis

The major products obtained were acetone-soluble oil (derived

from acetone free oil, wash oil, and aqueous phase solids), aqueous phase liquid, insolubles, and gas. The acetone free oil, on cooling, solidified and separated from the aqueous products. It was dried overnight in a vacuum water aspirator to lower moisture content below 20 %. The aqueous products were centrifused to recover the aqueous phase solids. Products that were not discharged were recovered by washing the unit with acetone. The acetone wash was then filtered in a 150 mL fritted glas filter of course grade. The wash oil was recovered by evaporating the acetone in a Buchi Rotary evaporator at 60-70°C under vacuum. The remaining acetone and moisture were removed by keeping the oil under vacuum for 2-3 days.

Moisture content of the oils and aqueous phase solids were determined using a Karl Fisher automatic titrator. Elemental (carbon,hydrogen,and oxygen by difference) analysis of the oils were determined by Guelph Laboratory Ltd. All samples were dried prior to analysis. The Waste Water Management Centre in Burlington determined the total organic carbon (TOC) content of the aqueous phase samples. Boiling point distributions of the oils were provided by BC Research.

2.3.5 RESULTS

Runs were made using wetted and non-wetted wood chips with steam at 330,335, 340, and 355°C. The reactor was preheated to 390-400°C before all runs. A summary of the operating conditions and products received are presented in Table I-II of Appendix 1. The temperature/pressure profiles of a typical run (#12) are presented in Figure 2, and the remaining sets obtained during these runs are provided in Appendix 2.

Material and carbon balances were made for run #6. These are given in Table I and II respectively. The distribution of carbon among the products is shown in Figure 3. Table III contains the elemental analysis of the oils from two runs (#5 and #6). The boiling point distributions of two oil samples are shown in Figure 4.

A series of runs were made with the steam injection time and steam generator (SG) water level constant at 7 s and 1.0 L respectively. The amount of aqueous products formed is shown as a function of the generator steam temperature in Figure 5. The acetone soluble and insolubles product distributions are presented graphically in Figures 6 and 7 respectively. The yields of acetone-soluble and insoluble material are depicted in Figure 8 and 9.

The first three set of runs were made for trial operation. Runs in which the wood chips were not completely converted (4, 10, 11, and 15) were not tabulated quantitatively. Run #5 was successful, but due to spillage, products were not recorded.

2.3.5 DISCUSSION

The runs presented here are steps towards the development of a continuous liquefaction process. The work done to date has been very successful. Oils were produced using steam generated at 335 - 355°C.

The typical temperature/pressure profiles of a run (#12) are shown in Figure 2. The following trends have been noticed:

(1) The middle of the cascade reactor (CR) has the highest initial temperature.

(2) The top of the CR rapidly drops in temperature immediately after the steam has been injected.

(3) The bottom of the CR heats up for about the first 15s and then cools over the next 15 s. This is followed by a gradual increase in temperature up to the 2 minutes mark.

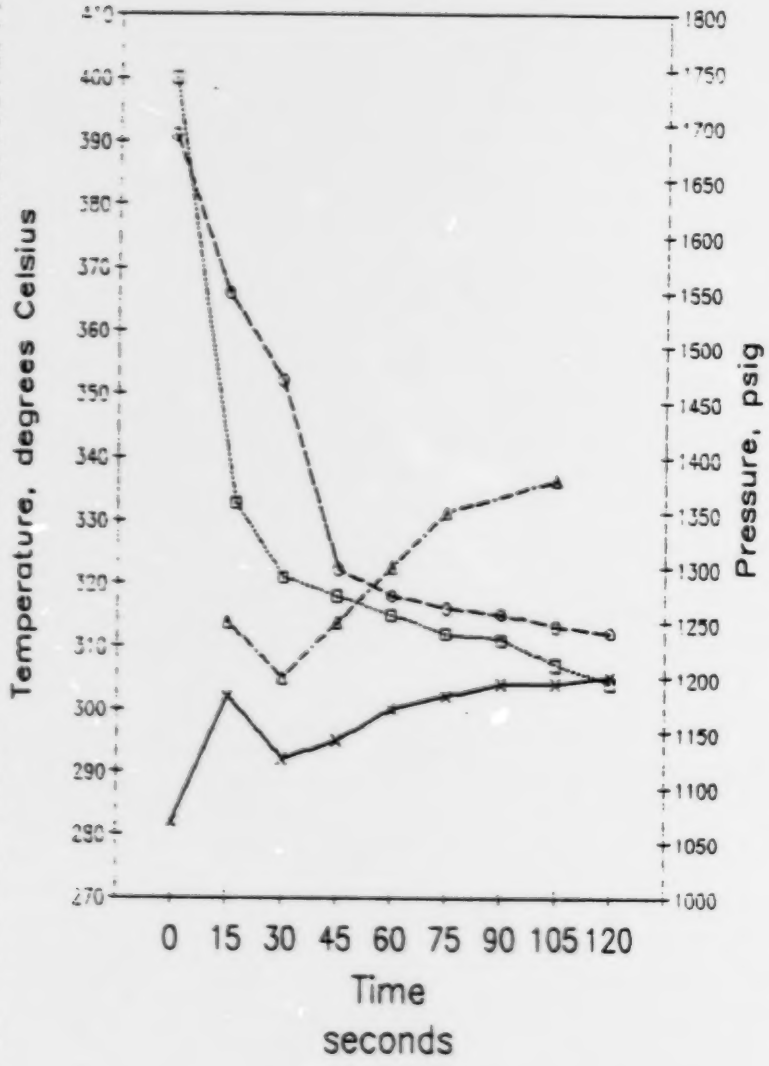
(4) The three reactor temperatures (top, middle, and bottom) converge around the 2 minutes mark.

(5) The reactor pressure goes up rapidly after a small drop.

FIGURE - 2

Temperature, Pressure Profiles

Steam for 7 Seconds
340°C, 2100 psig
1.0 L Water in SG



Run #12, WOOD NOT WETTED

These trends can be explained as follows:
The top and middle of the CR being hotter than the steam injected, are cooled rapidly. The bottom section, being colder than the steam, is heated initially. As cooler condensate collects in the bottom of the reactor, the temperature drops and then rises as heat is supplied to condensate from the reactor . The reactor pressure, as expected, appears to track the bottom temperature of the CR, but is slightly in excess of the expected vapour pressure due to product gas generation .

The results of a run (#6) are analysed and presented in Table I and Table II as mass and carbon balance respectively. This run was made with steam at 355°C and wood chips soaked with water for 20 minutes prior to liquefaction.

Table I shows that there is a loss of 24.8 g i.e. 7 % of the input mass. In the carbon balance (Table II), total carbon in the output (45.6 g) was found to be slightly higher (2.7 %) than the input (44.4 g). Considering the difficulties in cleaning the unit and determining the amount of water used and recovered, these results are within experimental error ranges. Figure 3 shows the distribution of carbon in the various product phases. The acetone-soluble oil yield for this particular run is 46 %, on a dry mass basis.

Table - I Mass Balance

		Grams	% Moisture
Input			
Solids :	Wood	100	8
Liquids :	Soaked Water	51	
	Steam Condensate	200	(estimate)
	(total= 351)		
Output			
Solids :	Acetone Free Oil	37.4	23
	Acetone Wash Oil	11.5	20
	Aqueous Phase Solids	10.8	60
	Insolubles:		
	From Basket	1.9	
	Filtered from Acetone Solubles	1.1	
Liquids:	Aqueous Phase	246.0	
Gases :		17.2	(estimate)
	(total = 326.2)		

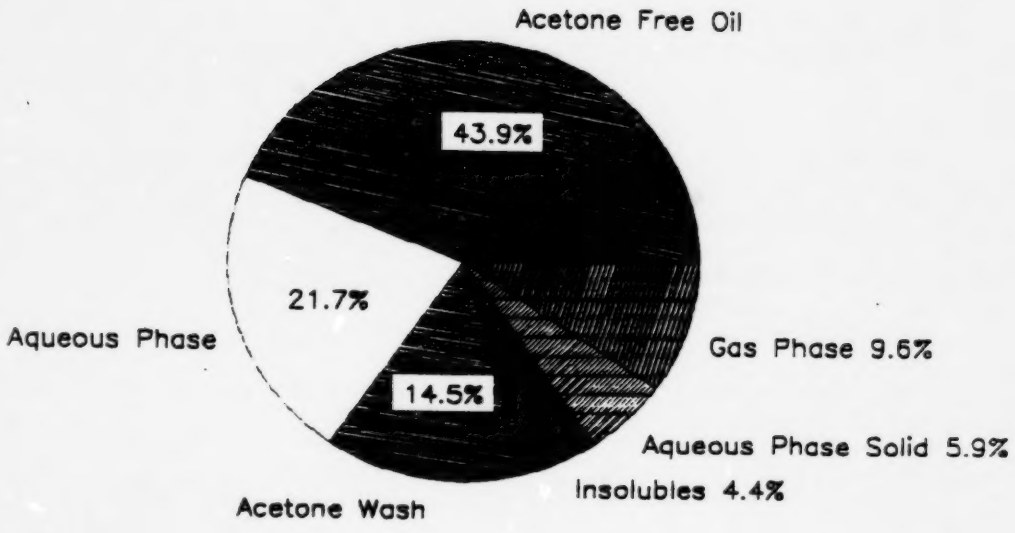
Table - II Carbon Balance (Dry Mass)

	Mass (g)	% Carbon	Total Carbon(g)
Input			
Wood Chips	92.0	48.3	44.4
Output			
Acetone Free Oil	28.90	69.1	20.0
Acetone Wash Oil	9.20	70.4	6.5
Acetone Insolubles	3.17	67.8	2.1
Aqueous Phase Solids	4.36	61.5	2.7
Aqueous Phase Liquid	252.00	40.4 g/l	9.9
Gases	17.20	28.3	4.4
			(total= 45.6)

FIGURE- 3

Wood Chips Liquefaction

Percent Carbon Balance
Product Distribution



Run # 6

Because the amount of aqueous products was always greater than the internal volume of the product letdown lock (122 mL), at least two discharges had to be made. As a result, some products remained in the reactor for at least 30 s (cooling time /discharge). Some char formed during this period, fouling the reactor and accumulating in the outlet valve.

The present letdown lock is being replaced with a large one (300 mL) to allow all the products to be collected in one discharge. The new vessel will have two thermocouples (top and bottom) and a pressure gauge, thus allowing monitoring of the internal temperatures and pressures.

Small particles trapped between the seat and stem of the reactor outlet valve became the source of a slow leak. After cleaning the valve body and tightening the stem, the rate of leakage was reduced.

It is believed that less material would accumulate and become charred if the AE port valve, currently used to discharge the products, was replaced with a ball valve. The straight through geometry of the ball valve, coupled with a larger letdown lock, would reduce the time needed to empty the reactor and minimize the opportunity for char formation.

Initially, the wood chips were wetted before each run. This was done to prevent charring of the wood while it was in the hot reactor prior to the steam injection. However, the amount of acetone-insolubles formed using non-wetted wood was actually less than those of similar runs using wetted wood chips (runs 7, 8, and 9). The amount of aqueous phase ejected from the reactor decreased, as expected, since surface water was no longer added, and also, less steam condensed in heating the surface water. Since there was no apparent need to add surface water to prevent charring, this practice was discontinued.

The first process variable to be studied was the steam injection time. It was reduced from 15 s to 7 s during runs 5 and 6, with all other variables essentially constant. No comparison of the product distribution was possible because of excessive loss of products during run # 5.

Elemental analysis revealed that the oil products from these two runs (#5 and #6) had approximately the same carbon, hydrogen and oxygen (by difference) contents (Table III). The oxygen content was higher than desired but similar to earlier findings. The boiling point distribution of the acetone free oils are identical within experimental error (Figure 4). It is reasonable to conclude, then, that reducing the steam injection time from 15 s to 7 s does not significantly change the oils produced.

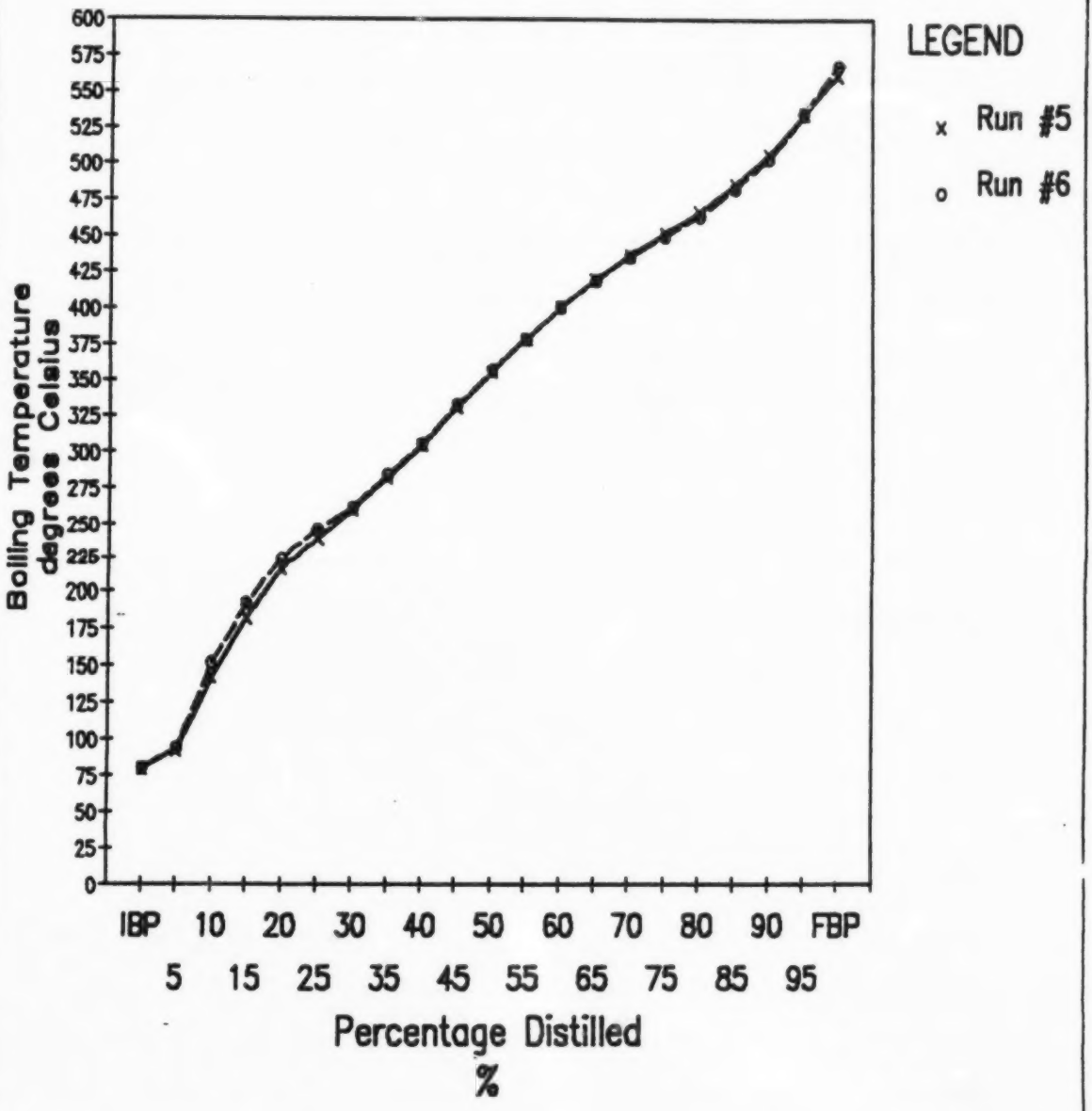
Table III : Carbon, Hydrogen and Oxygen Analysis of Products

RUN # 6	% Carbon	% Hydrogen	% Oxygen
Acetone Free Oil	69.1	6.04	24.86
Acetone Wash Oil	70.40	6.11	23.49
Aqueous Phase Solids	61.52		
Aqueous Phase Organics	40.4 grams / liter		
RUN # 5			
Acetone Free Oil	68.61	5.30	26.09
Acetone Wash Oil	67.75	4.91	27.34
Aqueous Phase Oil	66.94	5.53	27.53

FIGURE - 4

Boiling Point Distribution of Acetone Free Oils

by ASTM Method D2887-73



Data provided by BC Research

Further reduction of the steam injection time from 7 s to 2 - 3 s (run # 10) resulted in incomplete conversion of the wood chips. For this reason, the steam injection time was kept constant at 7 s for the remainder of the runs.

The steam temperature was varied from 330°C - 355°C with the steam injection time and steam generator level held constant at 7 s and 1.0 L respectively. Runs were made until the minimum steam temperature necessary for the liquefaction of the wood chips was found.

Steam at 330 C did not completely convert the wood chips to acetone-soluble oil. Almost all of the product remained in the basket as a moist semi- solid material (partially soluble in acetone), which hardened when dried. No runs were made with steam below 330°C.

The aqueous products distribution as a function of steam temperature is given in Figure 5. The amount of aqueous phase increased with steam temperature, as expected. At higher temperature, more steam is injected, because of the increased pressure. As a result, more condensate (aqueous phase) is formed.

The aqueous phase solids were thought to be an intermediate

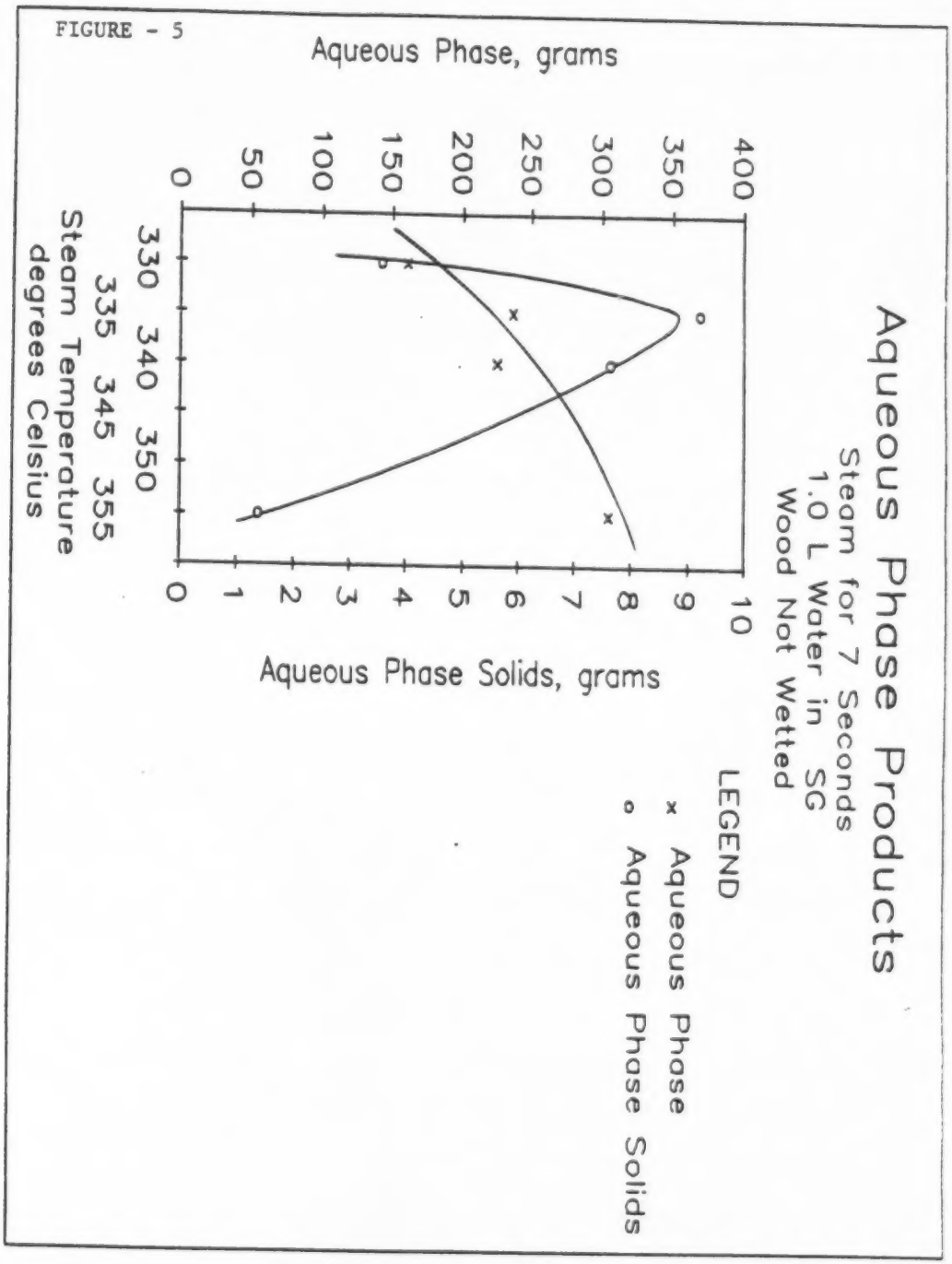

Aqueous Phase Products
Steam for 7 Seconds
1.0 L Water in SG
Wood Not Wetted
Aqueous Phase, grams
400
350
300
250
200
150
100
50
0
330 340 350
335 345 355
Steam Temperature
degrees Celsius
10
9
8
7
6
5
4
3
2
1
0
Aqueous Phase Solids, grams
LEGEND
x Aqueous Phase
o Aqueous Phase Solids

FIGURE - 5

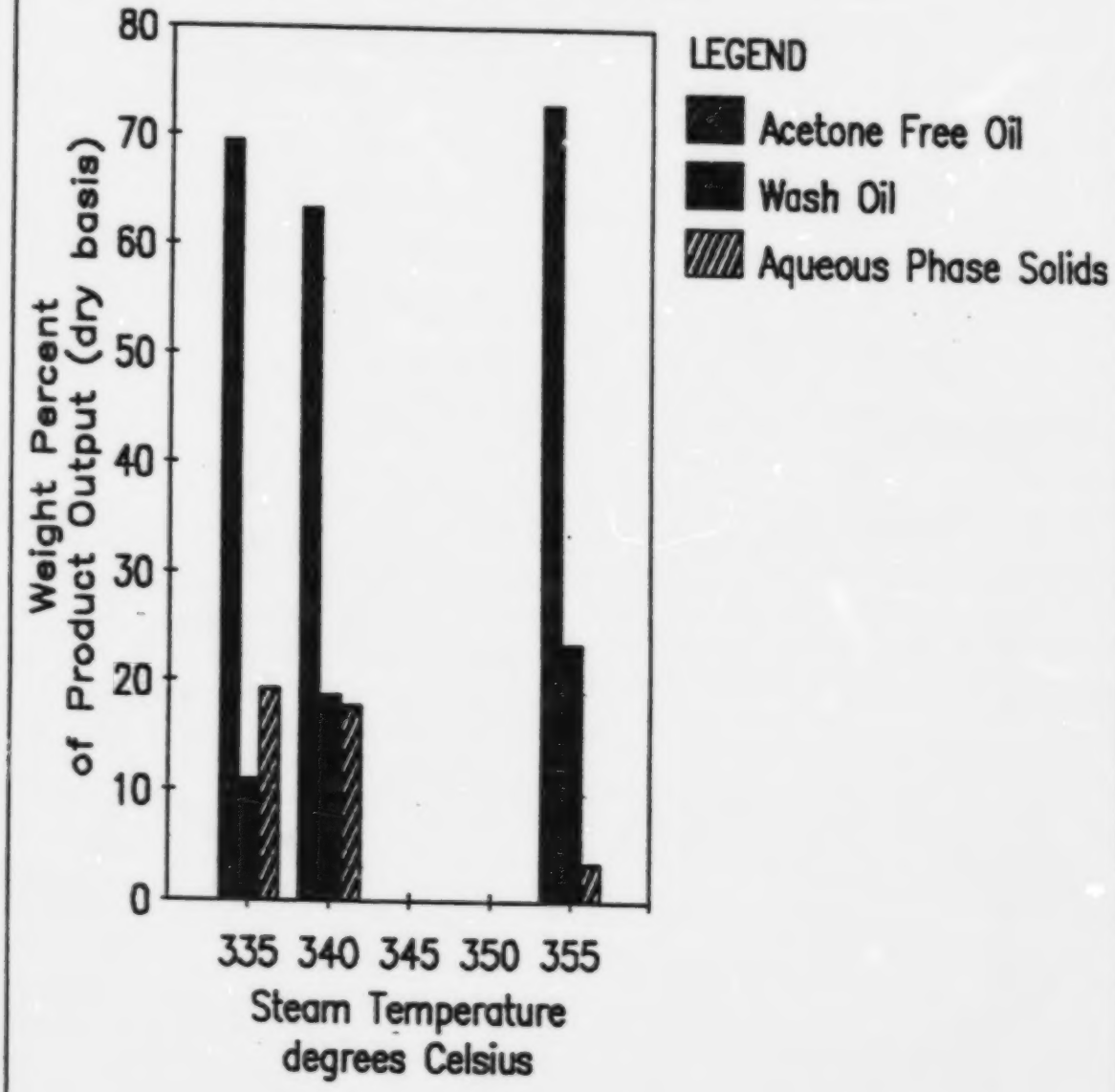
between the wood and oil. The decreased yield of aqueous phase solids at higher temperatures was accompanied by increased oil yields (Figure 6). Also the acetone insoluble fractions in acetone free oil and aqueous phase solids decreased with the increase of steam temperature (Figure 7). The aqueous phase solids darkened and became more soluble in acetone when heated.

It can be seen from Figures 8 and 9 that the yield of acetone soluble material is essentially constant at 43 %, based on wood input or 90 %, based on output. However, more of this material was found as oil at higher temperatures, as shown in Figures 6 and 7. Although using higher temperature steam does not necessarily increase the yield of acetone-soluble material, it does produce more of the desired products, ie. the oils. The amount of acetone insolubles decreased at higher steam temperatures. These results, we believe, justify using higher steam temperatures.

During the first few runs it was found that the amount of steam used was related to the initial water content and temperature of the steam generator. The steam generator was filled with 1 L of water before each run. The addition of a suitable level controller would make this unnecessary and allow sequential runs to be made, when used with the Milton Royal high pressure pump that is at our disposal.

Distribution of Acetone Soluble Products

Steam for 7 Seconds
1.0 L Water in SG
Wood Not Wetted



Insolubles and aqueous phase not included

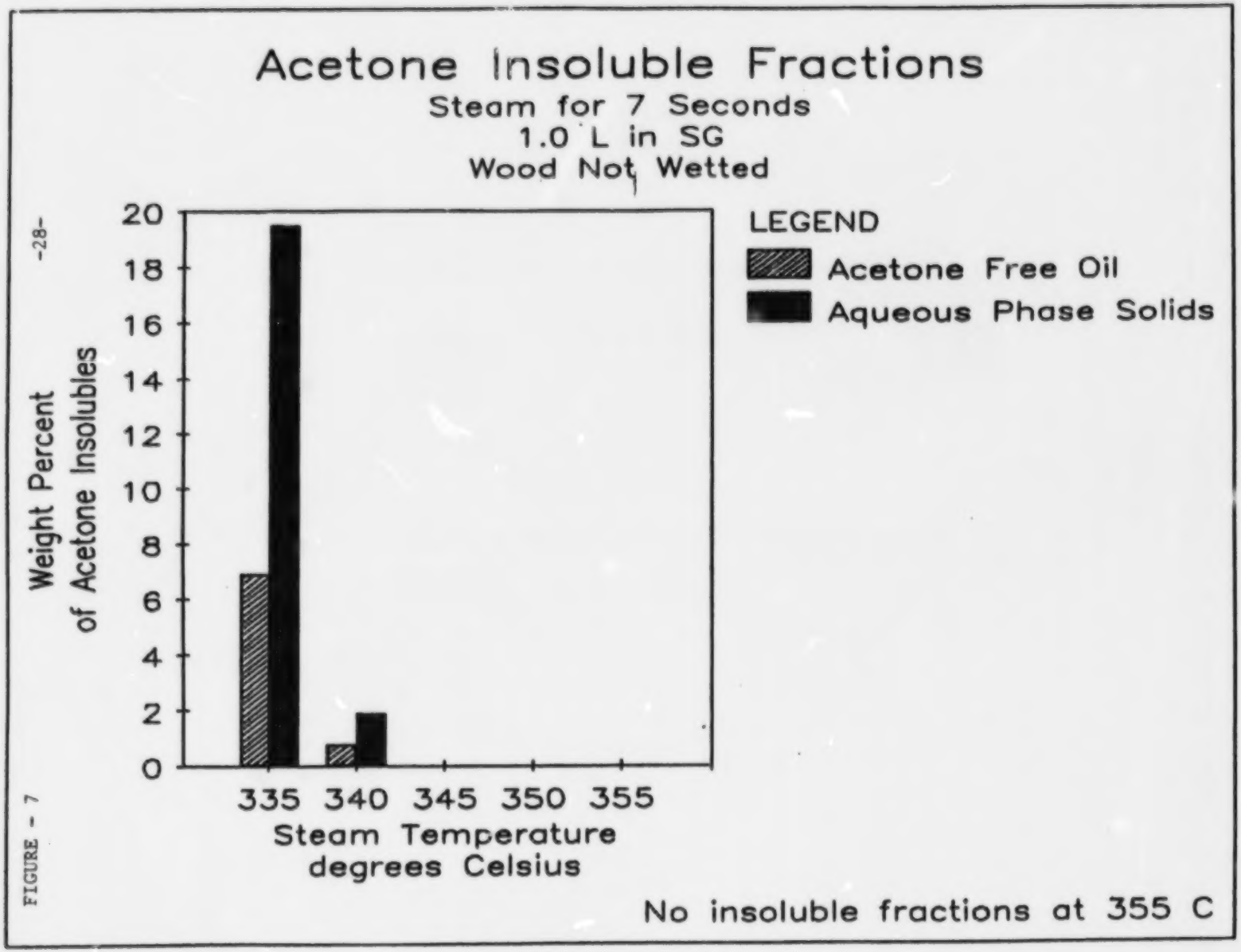
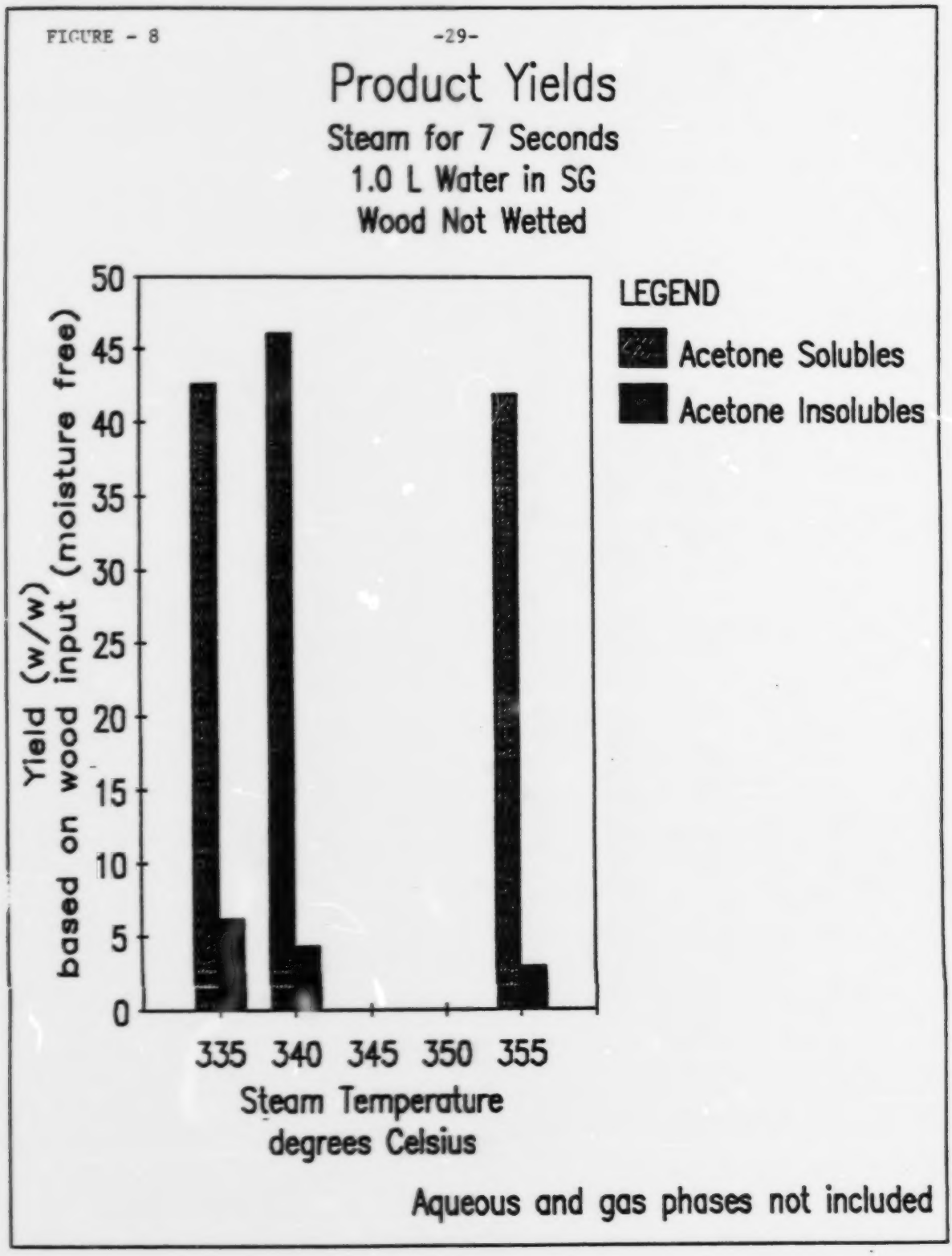
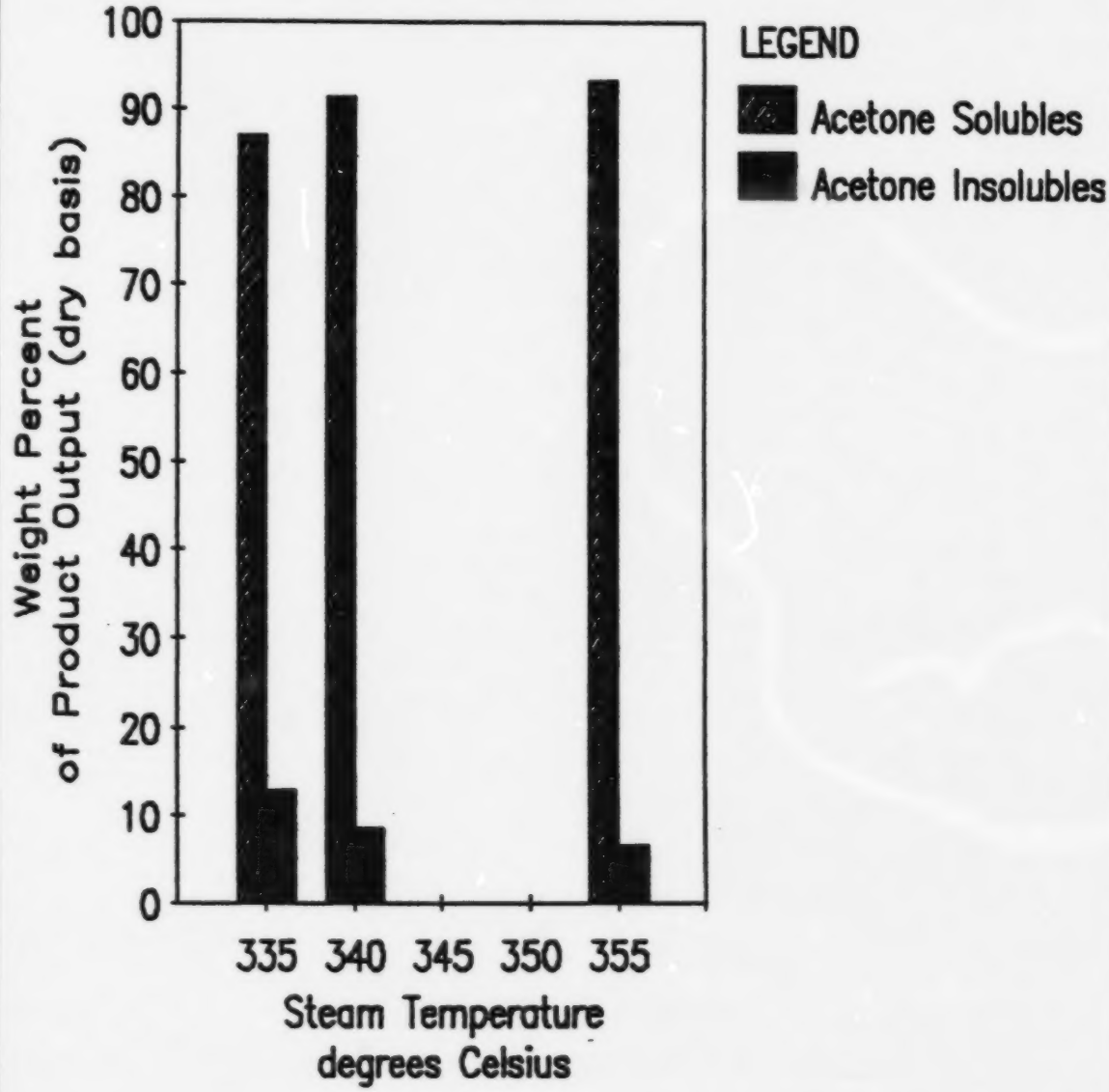

Acetone Insoluble Fractions
Steam for 7 Seconds
1.0 L in SG
Wood Not Wetted
LEGEND
Acetone Free Oil
Aqueous Phase Solids
Weight Percent
of Acetone Insolubles
0
2
4
6
8
10
12
14
16
18
20
335 340 345 350 355
Steam Temperature
degrees Celsius
No insoluble fractions at 355 C

FIGURE - 7


Product Yields
Steam for 7 Seconds
1.0 L Water in SG
Wood Not Wetted
LEGEND
Acetone Solubles
Acetone Insolubles
Yield (w/w)
based on wood input (moisture free)
0
5
10
15
20
25
30
35
40
45
50
335
340
345
350
355
Steam Temperature
degrees Celsius
Aqueous and gas phases not included

Acetone Soluble – Insoluble Products

Steam for 7 Seconds
1.0 L Water in SG
Wood Not Wetted



Aqueous phase not included

Lowering the initial water content to 0.5 L (keeping all other variables constant) resulted in more acetone insolubles being formed (run #16 vs run # 9) or incomplete conversion of the wood chips (run # 15 vs. runs # 13 & 14). It was found from run # 15 (steam at 335°C, .05 L water in steam generator) that the chips at the top of the basket were more converted to oil than those at the bottom.

Comparison of the results from runs # 13 and # 14, both having the same operating conditions, show that it is difficult to replicate results. The most difficult condition to duplicate from run to run was the temperature gradient in the reactor prior to the steam injection. The reactor temperature may have more of an effect on product yields than initially believed. The addition of a block heater at the reactor bottom showed improvement of the temperature gradient.

3.1 CONCLUSION

(a) A cascade autoclave system has been modified and operated successfully using IEA standard poplar chips.

(b) Acetone-soluble oil which softens just over 50°C, aqueous phase solids, aqueous phase, gas, and a small quantity of acetone insolubles were produced.

(c) The product distribution is a function of steam temperature, steam injection time, reactor temperature, reaction time, and water level in the steam generator.

(d) Analysis of a single run shows approximately a 46 % yield of acetone soluble products (oil), based on dry wood input. On an average, the oil yield is 43.6 % over the range of steam temperature studied (335°C - 355°C).

(e) Steam temperatures below 335°C result in incomplete conversion of the wood chips.

(f) Increasing the steam temperature from 335°C to 355°C decreases the yield of acetone insolubles and aqueous phase solids, while the amount of aqueous phase collected increases.

(g) Decreasing steam generator water content increases the yield of the acetone insolubles.

(h) Decreasing the steam injection time from 15 s to 7 s did

boiling point distributions. Further reduction to 2-3 s for steam injection resulted in incomplete conversion of the wood.

(i) It is not necessary to surface wet the wood prior to a run.

(j) The reactor temperature gradient, and amount of condensate formed were decreased after the addition of a block heater at the bottom of the reactor.

3.2 RECOMMENDATIONS

It is recommended that:

(a) The system be upgraded to allow continuous recording and storing of thermocouple temperatures.

(b) A pressure transducer should be incorporated in the reactor for monitoring pressure during the operation, and also as an safety feature.

(c) A new product cooler is necessary to collect the higher volume of aqueous phase products in one discharge.

(d) The reactor outlet valve should be replaced with a ball valve of high temperature and pressure ratings.

(e) A level controller should be installed in the steam generator to facilitate successive runs.

(f) More runs be made to study the use of green and dry wood. In addition the effect of chip size should be investigated. Chips up to 3.5 cm diameter and 64 cm long can be fed to the cascade reactor.

3.3 BIBLIOGRAPHY

1. Boocock, D.G.B., "Construction of a Cascade Autoclave System for the Liquefaction of Wood Chips", Report of DSS Contract File No. 05SV 23216-6191, Bioenergy Development Program, Renewable Eenergy Branch, Energy, Mines and Resources, Ottawa, Ontario, 1986 (17 pp).

2. Porretta, F., "The Rapid Aqueous Pyrilysis of Poplar Chips", M.A.Sc. Thesis,Department Of Chemical Engineering, University of Toronto, 1983.

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4. Boocock, D.G.B., and Mackay,D., "Further Development of Processes for the Conversion of Wood to Liquid Fuels through Operation of a Continuous/Semi-Continuous Liquefaction

Unit", Report of Contract File # 24 SU. KN107-2-4069 for Renewable Energy Division, National Research Council, Ottawa, Ontario, 1983 (23 pp).

5. Boocock, D.G.B., "Further Studies on Wood Liquefaction through Operation of a Continuous/Semi-Continuous Wood Liquefaction Unit", Report of Contract File #24SU.23216-3-6143 for Renewable Energy Division, Energy, Mines and Resources, Ottawa, Ontario, 1984 (25 pp).

6. Beckman,D.,and Boocock, D.G.B., "Liquefaction of Wood by Rapid Hydropyrolysis", Can. J. Chem.Eng.,61,802-808,1983.

7. Boocock, D.G.B., and Sherman, K.M., "Further Aspects of Powdered Poplar Wood Liquefaction by Aqueous Pyrolysis", Can.J.Chem.Eng., 62, 627-733,1985.

A P P E N D I X 1

Table-1 OPERATING CONDITIONS OF RUNS

RUN #	Wood Condition	Steam Temp. (C)	Steam Injection Time (s)	Reaction Time (min.)	Product Cooling Time (s)	Water in Steam Generator (L)	Reactor Temperature (T2-T4-T5) (C)
6	Wet	355	7	2	30	.65	281-390-400
7	Wet	355	7	2	30	1	277-390-396
8	Wet	355	7	2	30	1	277-388-400
9	dry	355	7	2	30	1	282-389-402
10*	Dry	355	2-3	2	30	1	280-396-398
11*	Dry	330	7	2	30	1	301-391-400
12	dry	340	7	2	30	1	282-391-400
13	Dry	335	7	2	30	1	291-397-400
14	Dry	335	7	2	30	1	298-398-406
15*	Dry	335	7	2	30	.50	290-395-405
16	Dry	355	7	2	30	1	292-393-405

(*)- Incomplete Runs

Table-2 PRODUCTS

RUN #	Acetone Free Oil gm	Acetone Wash Oi gm	Aqueous Solids gm	Aqueous Phase gm	Acetone Solubles gm	Acetone Insolubles gm
6	28.9	9.2	4.4	252	42.1	3.3
7	22.9	11.5	2.8	365	36.9	3.3
8	19.3	13.3	3.3	340	35.6	3.5
9	28.5	9.2	1.4	305	39.0	2.8
12	26.0	7.9	7.6	225	41.9	3.9
13	31.9	5.5	11.3	192	44.9	5.4
14	26.2	3.1	7.1	280	32.8	NA
16	31.0	7.1	1.7	251	43.4	3.7

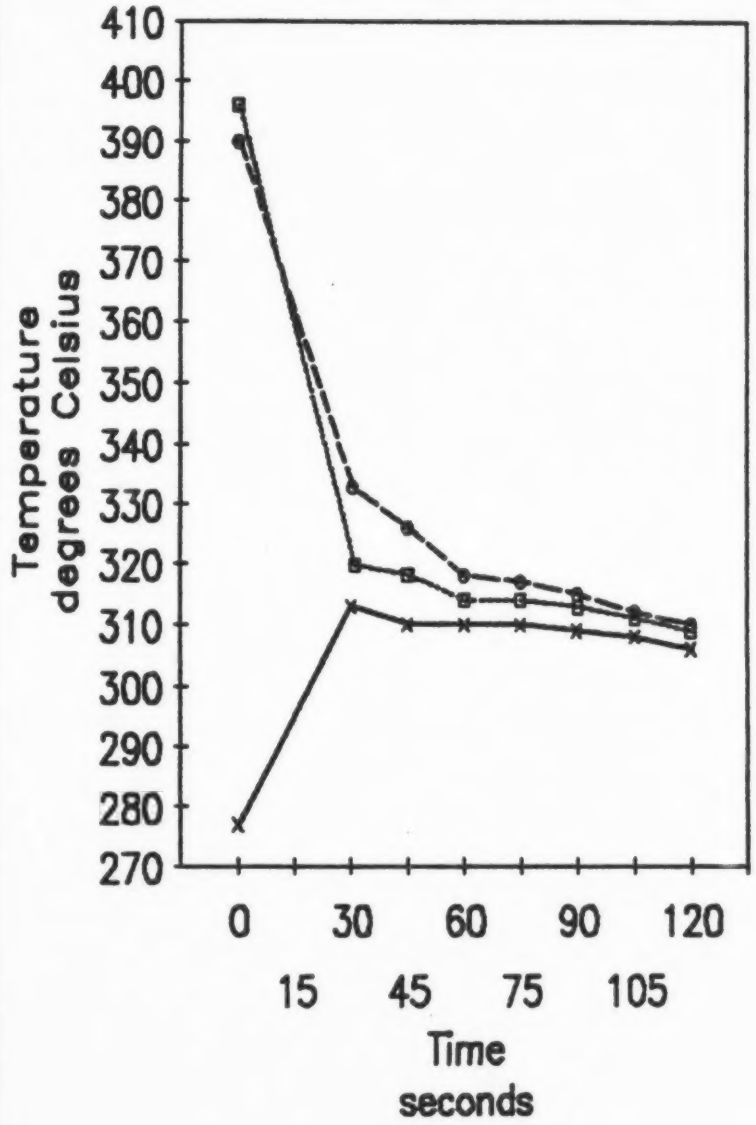
Note: All the Figures are on Dry Basis

APPENDIX 2

TEMPERATURE / PRESSURE PROFILES

Temperature Profiles

Steam for 7 Seconds
355°C, 2550 psig
1.0 L Water in SG



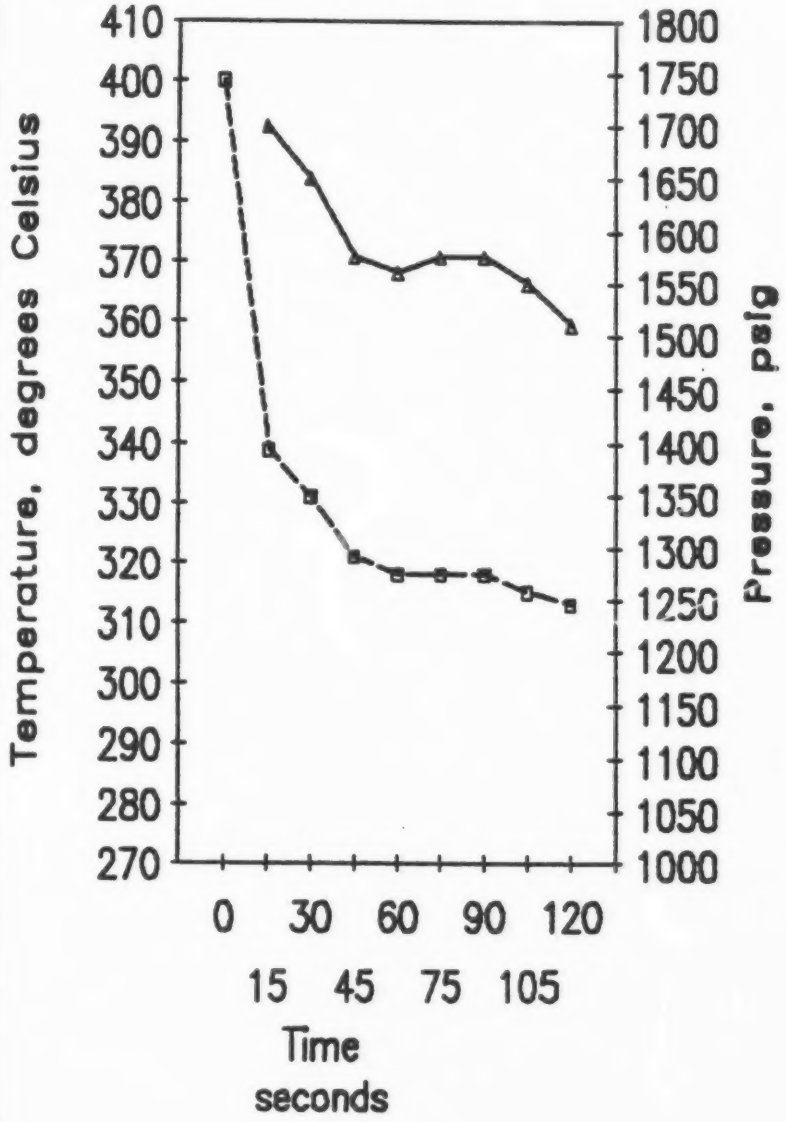
LEGEND

x T2 bottom of CR
o T4 middle of CR
□ T5 top of CR

Run #7, WOOD WETTED

Temperature, Pressure Profiles

Steam for 7 Seconds
355°C, 2510 psig
1.0 L Water in SG

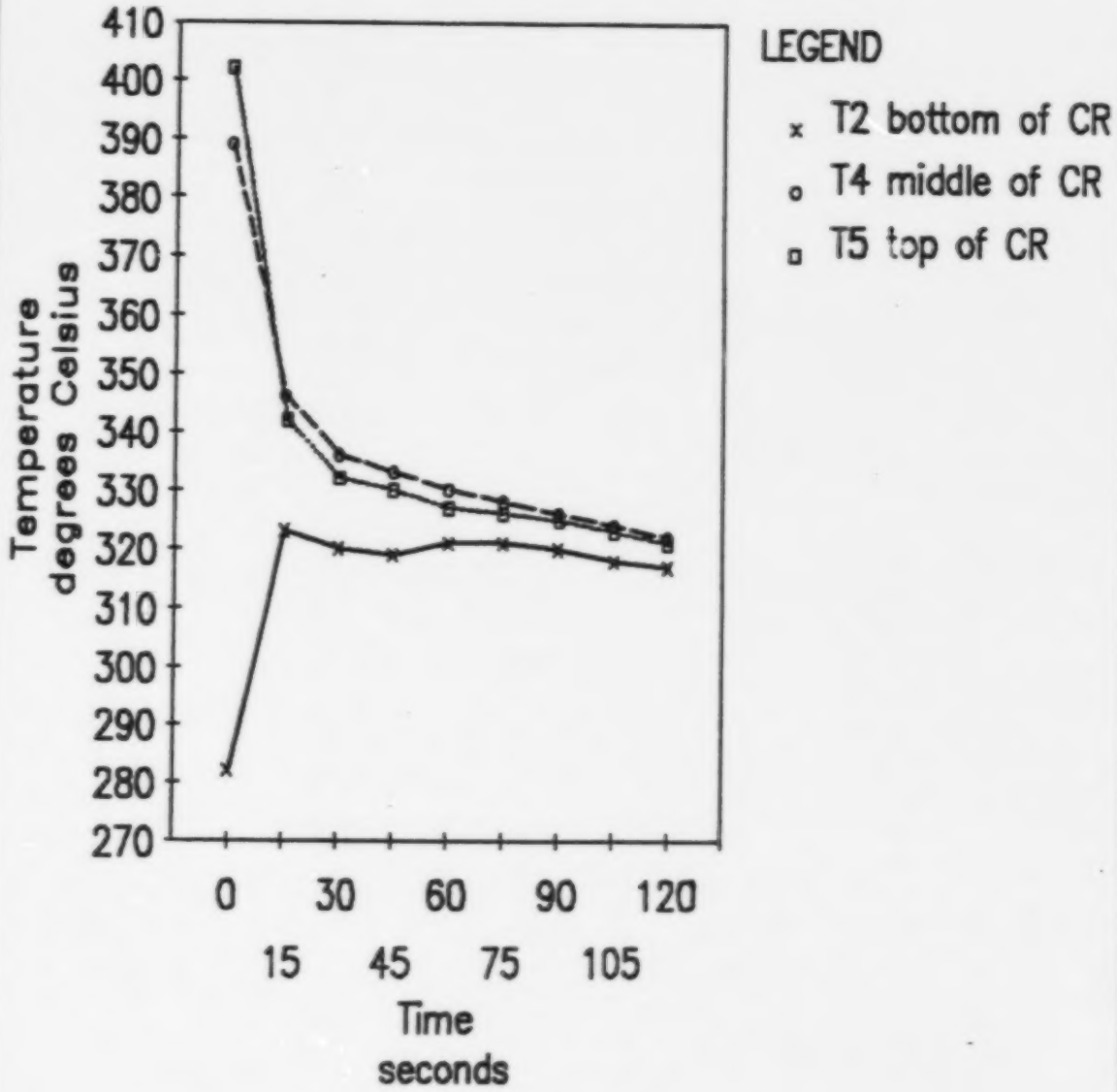


Run #8, WOOD WETTED

FIGURE - 12

Temperature Profiles

Steam for 7 Seconds
355°C, 2520 psig
1.0 L Water in SG

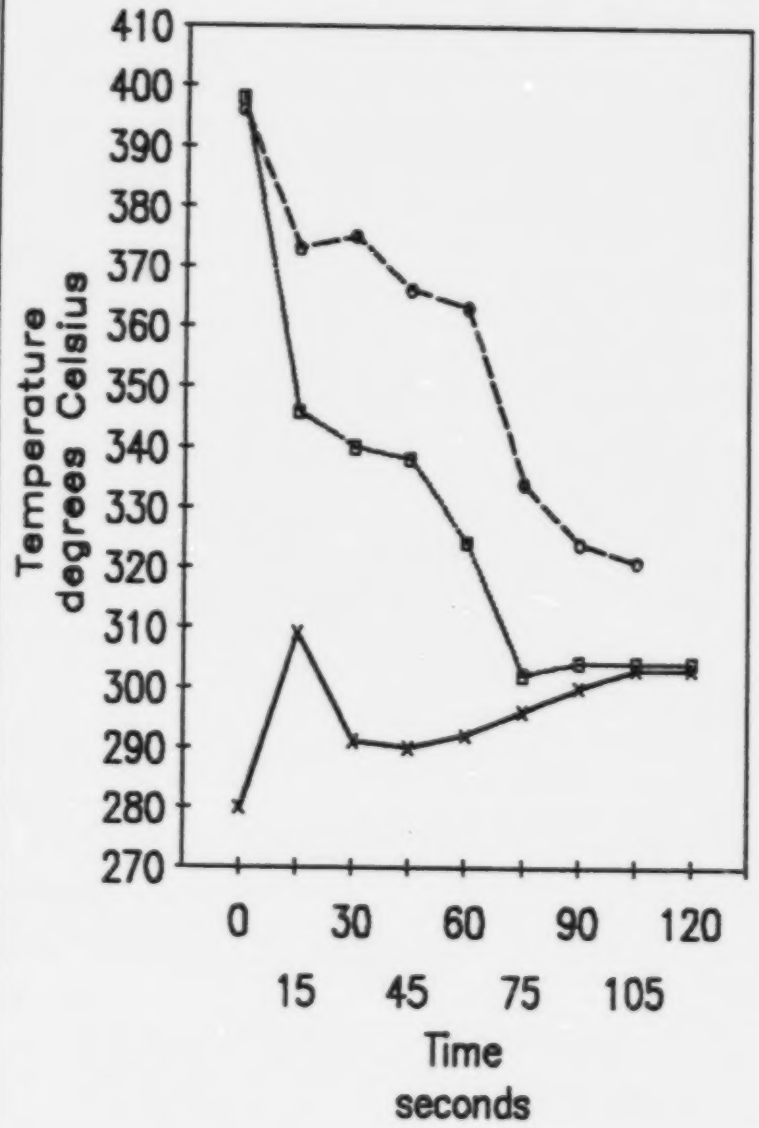


Run #9, WOOD NOT WETTED

FIGURE -13

Temperature Profiles

Steam for 2 – 3 Seconds
355°C, 2550 psig
1.0 L Water in SG



LEGEND

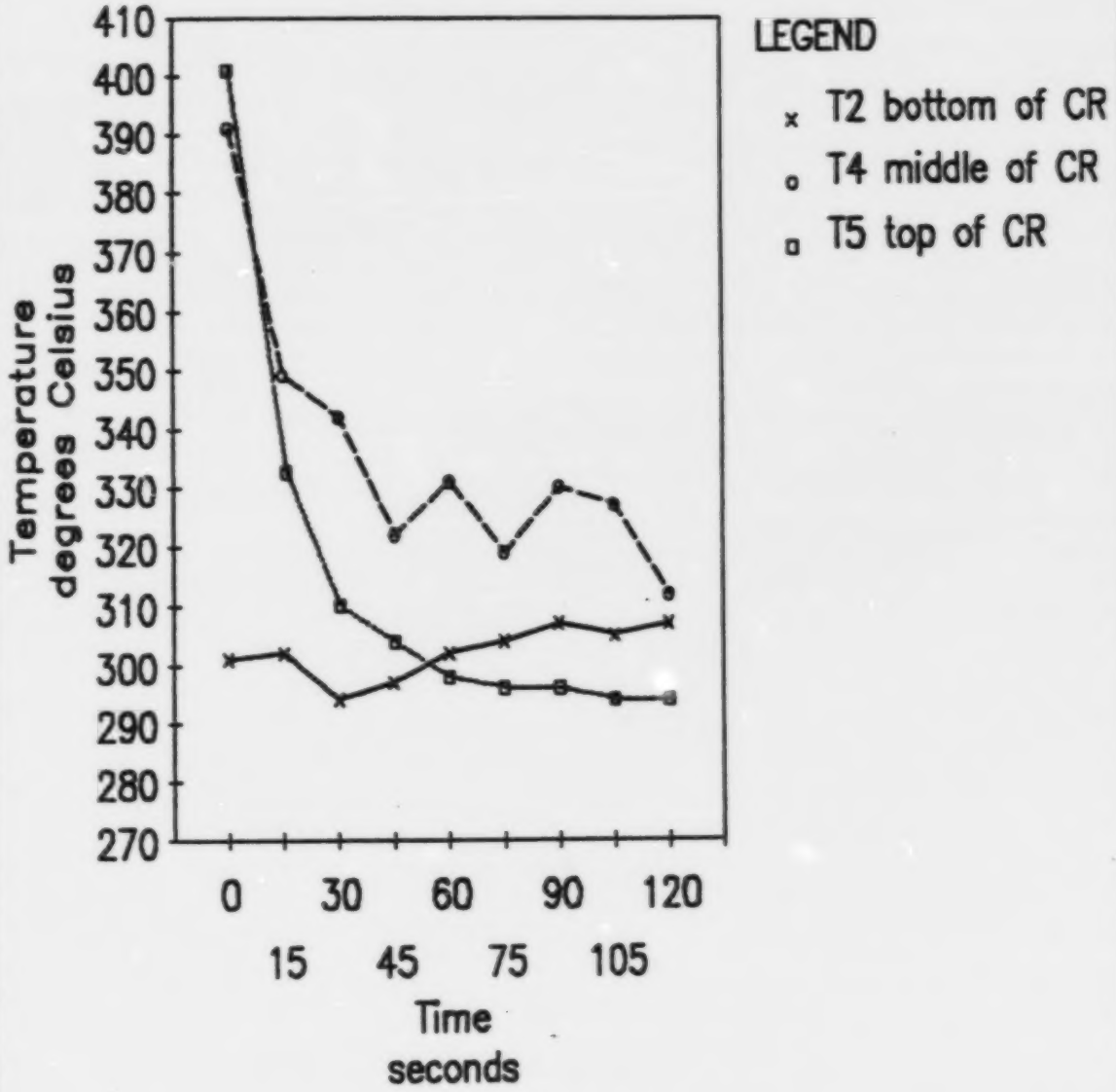
- x T2 bottom of CR
- o T4 middle of CR
- □ T5 top of CR

Run #10, WOOD NOT WETTED

FIGURE -14

Temperature Profiles

Steam for 7 Seconds
330°C, 1890 psig
1.0 L Water in SG

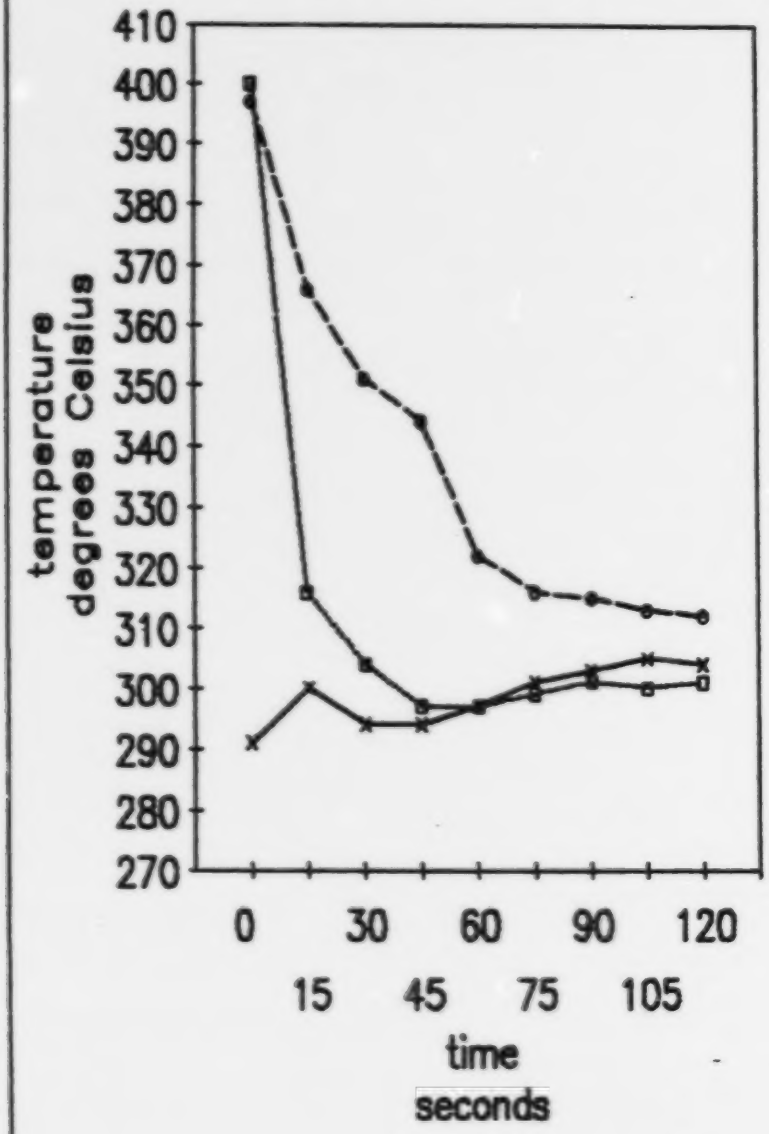


Run #11, WOOD NOT WETTED

FIGURE - 15

Temperature Profiles

Steam for 7 Seconds
335°C, 2000 psig
1.0 L Water in SG



LEGEND

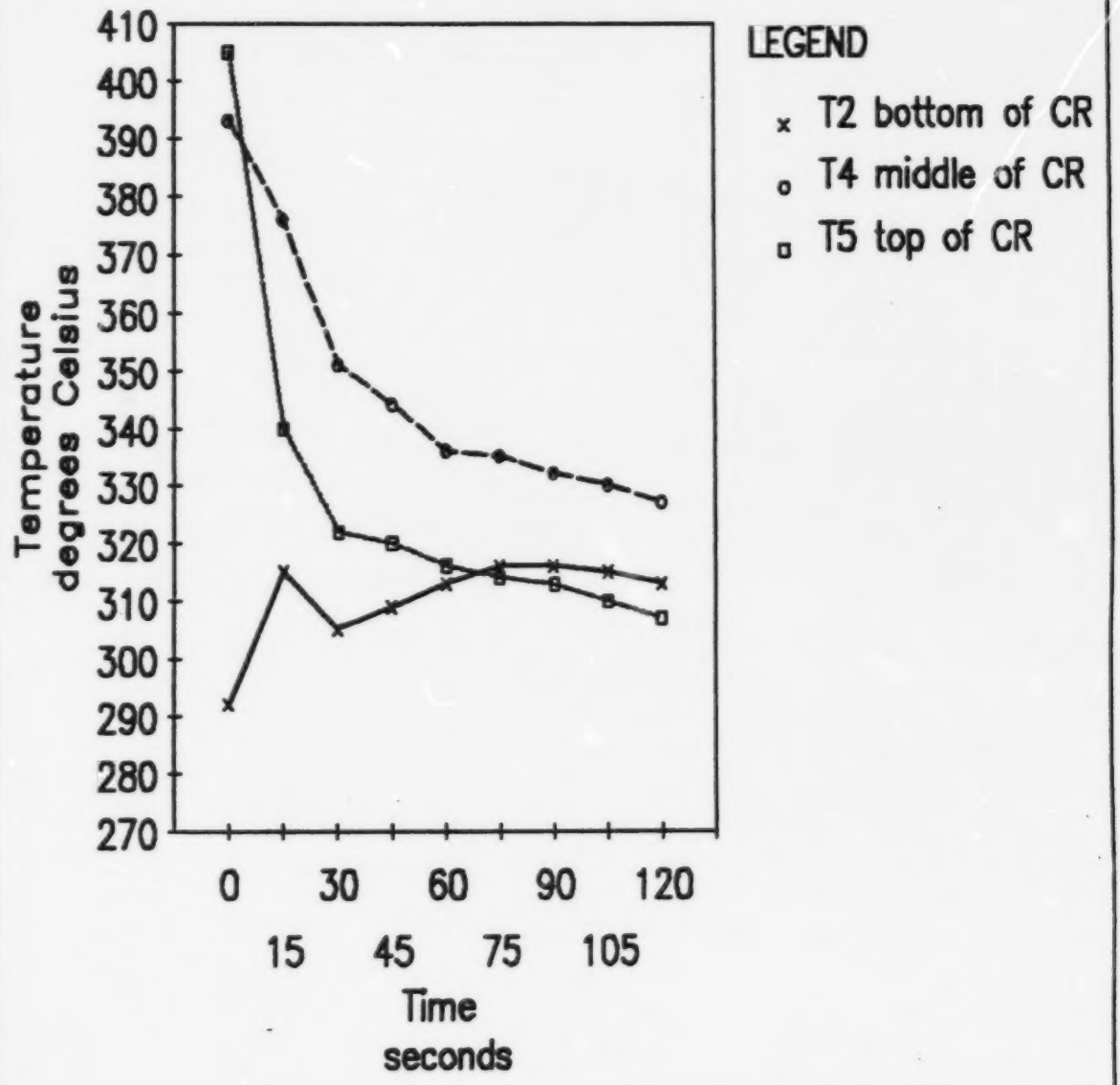
- x T2 bottom of CR
- o T4 middle of CR
- □ T5 top of CR

Run # 13, WOOD NOT WETTED

FIGURE - 16

Temperature Profiles

Steam for 7 Seconds
355°C, 2550 psig
0.5 L in SG



Run #16, WOOD NOT WETTED